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Firefighter's occupational exposure to $PM_{2.5}$ and Polycyclic Aromatic Hydrocarbons

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ABSTRACT: This study collected the personal $PM_{2.5}$ air fraction in fifteen healthy and no-smoking firefighters during their normal shift inside four Portuguese fire stations. Indoor $PM_{2.5}$ levels varied between 0.05 to 1.04 μg/m^3. Polycyclic Aromatic Hydrocarbons (PAHs) are known for their ubiquity and toxicity, being some of them classified as carcinogenic and possible carcinogens to humans. Firefighters' personal $PM_{2.5}$-bound total PAH concentrations ranged between 35.8 to 294 ng/m^3 with total carcinogenic PAHs accounting with 12% to the total PAHs. Benzo[a]pyrene, the PAH biomarker of carcinogenicity, was detected in levels ranging from 6.74×10^{-2} to 1.00 ng/m^3.

1 INTRODUCTION

Firefighting is one of the most hazardous yet the least studied occupations in terms of exposures and their relationship to occupational diseases. Firefighters are chronically exposed to complex mixtures of particles, smoke and products of incomplete combustion which contain a high number of substances such as carbon monoxide and dioxide, nitrogen oxides, respirable Particulate Matter (PM), carbonyls (methanol, formaldehyde, 2,3-butanedione, acetaldehyde, acetone, methylethylketone), volatile (benzene, toluene, acetonitrile), and semi-volatile organic compounds including polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, Polycyclic Aromatic Hydrocarbons (PAHs), nitro-PAHs, and nitro-PAHs lactones (Estrellan & Lino 2010; Lemieux 2004; Lewtas 2007; Reisen et al. 2006).

Particulate matter is a mixture of solid or solid/liquid particles suspended in air that vary in size, shape, origin, and chemical composition (WHO 2006). PM with aerodynamic diameter lower than 2.5 μm, $PM_{2.5}$, is among the most relevant size fractions because it can reach lower parts of respiratory tract where it deposits in the conducting air ways and gas exchange regions of lungs. PM is originated from a variety of outdoor natural (pollen, spores, bacteria, plant, animal debris, and suspended crustal materials) and anthropogenic (combustion of fossil fuels, biomass burning, and ammonia emissions from agricultural operations) sources (WHO 2006). Indoor sources of PM include human activities such as cleaning, cooking, and combustion processes such as wood and fossil fuel burning, or tobacco smoke.

PAHs are one of the most relevant pollutants that are found adsorbed to PM surface. PAHs are classified as persistent organic pollutants (WHO 2013) with sixteen of them being regarded as priority pollutants by the USA Environmental Protection Agency (USEPA 2005). Among the 16 USEPA priority PAHs, benzo[a]pyrene is the only compound classified as carcinogenic to humans (i.e. group 1) by the International Agency for Research on Cancer. Naphthalene, benz[a]anthracene, benzo[b]fluoranthene, benzo[j]fluoranthene, benzo[k]fluoranthene, chrysene, and indeno[1,2,3-c,d]pyrene are classified as possibly carcinogenic to humans (group 2B; IARC 2002, 2010). Additionally, some studies have also included dibenzo[a,l]

pyrene and dibenz[a,h]anthracene because they are regarded as probable carcinogens to humans due to their higher carcinogenic potency than benzo[a] pyrene (Okona-Mensah et al. 2005; Oliveira et al. 2015). The presence of PAHs in the environment is primarily due to emissions from incomplete combustion of carbon fuels from natural, industrial, commercial, vehicular, and residential sources. When they are not actively suppressing fires onduty firefighters stay, live and work at their fire stations. Scarce information is available regarding firefighters occupational exposure at fire stations.

The present work aims to assess firefighters' personal exposure to indoor $PM_{2.5}$ and $PM_{2.5}$-bound PAHs at four Portuguese fire stations.

2 MATERIAL AND METHODS

2.1 *Sampling*

Fifteen healthy and no-smoking firefighters were asked to wear a personal air pump during four consecutive hours during their regular work shift indoors at four fire stations located in Bragança, north of Portugal. $PM_{2.5}$-bound PAHs were collected on polytetrafluoroethylene membrane filters with polymethylpentene support ring (2 µm porosity, SKC Ltd., United Kingdom) by constant flow sampler. $PM_{2.5}$ masses were determined gravimetrically according to Slezakova et al. (2014). Briefly, the initial mean mass of the blank filter was subtracted from the final mean mass of the exposed filter; the difference was then divided by the total volume of air that passed through the filter (at 25°C and 101.3 kPa). After the sampling, filters were stored in a freezer (–20°C) before consequent chemical analysis.

2.2 *PAHs extraction and quantification*

Sixteen USEPA priority PAHs, namely naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene, and indeno[1,2,3-cd]pyrene, as well as dibenzo[a,l] pyrene and benzo[j]fluoranthene (recommended by EU Directive 2004/107/EC) were extracted from $PM_{2.5}$ by microwave assisted extraction according to the previously validated methodology (Castro et al. 2009, 2011). Extracts were analyzed using a Shimadzu LC system (Shimadzu Corporation, Kyoto, Japan) equipped with a LC–20 AD pump, DGU–20 AS degasser and photodiode array SPD–M20 A (PAD) and fluorescence RF–10 AXL (FLD) detectors on line. Separation of the compounds was performed in a C18 column (CC 150/4 Nucleosil 100–5 C18 PAH, 150 × 4.0 mm; 5 µm particle size; Macherey–Nagel, Duren, Germany) maintained at room temperature (20 ± 1ºC). The total run time was 40 min with a flow rate of 0.8 mL min^{-1}. The injected volume was 15.0 µL. Individual PAH identification was carried out by comparison of their retention times with those of their respective standards. External calibrations with PAHs mixed standards, using at least 6 calibration points, were performed. Analytical blanks and standards were analyzed daily and regularly. Each analysis was performed at least in triplicate.

3 RESULTS AND DISCUSSION

3.1 *$PM_{2.5}$ concentrations*

$PM_{2.5}$ exposure levels of firefighters in the characterized four Portuguese fire stations ranged between 0.05 to 1.04 µg/m^3.

Studies concerning firefighters' exposure to $PM_{2.5}$ are limited, particularly at fire stations. A study conducted in American wildland firefighters at non prescribed forest burn days assessed personal $PM_{2.5}$ concentrations ranging from 9 and 43 µg/m^3 during a work shift of 7 to 12 hours (Adetona et al. 2011). More recently, a study conducted also in American firefighters reported $PM_{2.5}$ concentrations ranging between 18 and 155 µg/m^3 at two firehouses (Baxter et al. 2014). In this work, the determined $PM_{2.5}$ concentrations were well below the values reported by those studies.

Regarding occupational exposure, the National Institute for Occupational Safety and Health (NIOSH) defined a permissible exposure limit of 15 and 5 µg/m^3 for total and respirable particles not otherwise regulated, respectively (NIOSH 2007). Firefighters' personal exposure to $PM_{2.5}$ inside Portuguese fire stations was below those guidelines.

3.2 *PAH concentrations*

In this study, $PM_{2.5}$-bound PAHs were evaluated in Portuguese firefighters' personal air. Individual PAHs namely naphthalene, acenaphthene, fluorene, and phenanthrene were detected in all the samples while acenaphthylene, benzo[b+j]fluoranthene, and benzo[g,h,i]perylene were detected in more than 80% of $PM_{2.5}$ filters. Chrysene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene were detected in less than 15% of the samples. Among the 18 analyzed PAHs, dibenzo[a,l]pyrene was the only compound that was never detected in the firefighters personal air samples.

Overall, total PAH concentrations ranged between 35.8 to 294 ng/m^3. Acenaphthylene,

acenaphthene, naphthalene were the most abundant compounds, accounting for almost 88% of the total PAHs. Other predominant PAHs were, by descending order: dibenz[a,h]anthracene, phenanthrene, and benzo[g,h,i]perylene. Together these six PAHs represented 97% of total PAHs.

As described in previous studies (Oliveira et al. 2015; Slezakova et al. 2014), in air PAHs are distributed between gaseous (predominantly compounds with 2–3 rings) and particulate phases (mainly PAHs with 4 or more aromatic rings). At the four Portuguese fire stations, $PM_{2.5}$ indoor fraction presented significantly higher concentrations of acenaphthylene and acenaphthene. No specific occurrences that could justify the high prevalence of these two PAHs in the indoor $PM_{2.5}$ phase were found. A possible explanation to this evidence may be the contribution from some particular emission source inside fire stations.

Several countries have set occupational exposure limits for coal-tar pitch volatiles or particulate PAHs (IARC 2002). Those reference values are typically based on the benzene—or cyclohexane-soluble matter of the particulates present in air which includes benz[a]anthracene, benzo[b]fluoranthene, chrysene, anthracene, benzo[a]pyrene, phenanthrene, acridine or pyrene. The Agency for Toxic Substances and Disease Registry recommended an airborne exposure limit of 0.1 mg/m^3 for coal tar pitch volatiles during a working day (ATSDR 2015). Portuguese firefighters' personal exposure to PAHs was well below those limits. Additionally, the American Conference of Governmental Industrial Hygienists states that, for any substance with no numerical threshold limit value (but designated as a suspected human carcinogen), worker exposure by all routes should be carefully controlled to levels as low as possible (ACGIH 2010).

Only two studies were found in the literature regarding firefighters exposure to PAHs at fire stations. Shen et al. (2015) focused on dust samples collected from different vacuum cleaner bags, which were used to routinely clean twenty Californian fire stations. Authors reported total PAHs concentration of 4124 ng/g in dust, being pyrene, benzo[ghi]perylene, fluoranthene, and chrysene the most predominant PAHs (Shen et al. 2015). Baxter et al. (2014) conducted a study in two different metropolitan fire stations located in Cincinnati, USA. Air monitoring was performed in the fire truck bay, equipment storage area, kitchen/common area, and in sleeping quarters during a period of 8-hours on a single day. Among the seventeen screened PAHs, only naphthalene was found in one fire station, with mean concentrations of 9.22 µg/m^3 and 9.24 µg/m^3 at the kitchen and truck bay, respectively (Baxter et al. 2014). Mean concentration of naphthalene was 9.69 ng/m^3 (2.03–14.3 ng/m^3) at four Portuguese fire stations which was similar to those reported by Baxter et al. (2014). The concentrations of naphthalene in Portuguese fire stations were well below the short-term exposure limit of 11 mg/m^3 over a period of 15-minutes of exposure designated by the US National Institute for Occupational Safety and Health (NIOSH 2007).

Due to the presence of aromatic rings, PAHs present high toxicity, mutagenicity and carcinogenic characteristics (IARC 2002, 2010). Benzo[a]pyrene, the biomarker of carcinogenicity, was detected in 67% of the samples with concentrations ranging between 6.74×10^{-2} and 1.00 ng/m^3 (mean of 0.23 ng/m^3) in the indoor air of fire stations. Overall, total concentrations of carcinogenic PAHs ranged from 2.89 to 23.7 ng/m^3 (mean of 20.9 ng/m^3) and accounted with 12% for the total PAHs.

4 CONCLUSIONS

This work provides relevant information regarding occupational exposure of Portuguese firefighters to $PM_{2.5}$ and $PM_{2.5}$-bound PAHs in the indoor air of four fire stations. Globally, $PM_{2.5}$ concentrations were well below the Portuguese guideline and as a consequence might not represent significant risks for firefighters health. Total $PM_{2.5}$-bound PAHs ranged between 35.8 and 294 ng/m^3 and total concentrations of carcinogenic PAHs accounted with 12% for the total PAHs. Since some PAHs have been reported to possess reproductive, developmental, hemato-, cardio-, neuro-, and immuno-toxicities in human and laboratory animals (ATSDR 1995), more studies regarding firefighters occupational exposure to PAHs are needed in order to better characterize the respective exposures.

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